Chapter 18
Chemical Reduction/Oxidation

18-1. General

The process of reduction/oxidation (redox), its applications, and resulting waste streams are described in the chapter's first section. The second portion of the chapter is a hazard analysis with controls and control points listed.

18-2. Technology Description

a. Process.

Redox reactions chemically convert hazardous contaminants to less hazardous or non-hazardous compounds that are more stable, less mobile, less toxic, or inert. This is accomplished by chemical reactions that involve electron transfer (and usually other chemical groups) from one reactant (oxidized compound) to another compound (reduced compound).

As shown in Figure 18-1, excavated soil is screened and oversized rejects are combined with the sludge for disposal. Water is added to the screened soil, and the slurry is transferred to a reactor, where reagents (such as ozone, hydrogen peroxide, hypochlorites, chlorine, or chlorine dioxide) are added to react with targeted constituents. The reagent/soil mixture is transferred to a separator, where excess reagent is removed and recycled back into the reactor. The treated soil is washed and dewatered. Water from the dewatering process is recycled back to the soils washer. The dewatered sludge is combined with oversized rejects for disposal.

b. Applications.

In addition to soils treatment, chemical redox is an established technology for the disinfection of drinking water and wastewater. Ultraviolet (UV) oxidation is an example of a UV-stimulated version of this treatment approach. The technology can be applied to both liquid and solid wastes.

The target contaminants for redox reactions are usually inorganic species, especially cyanide or chromium-containing wastes, but can also be used for phenols and other readily oxidized organics. The technology is less effective for non-halogenated volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), fuel hydrocarbons, pesticides, and high contaminant concentrations. Oil and grease in the waste should be minimal to prevent excessive side reactions and increase process efficiency.

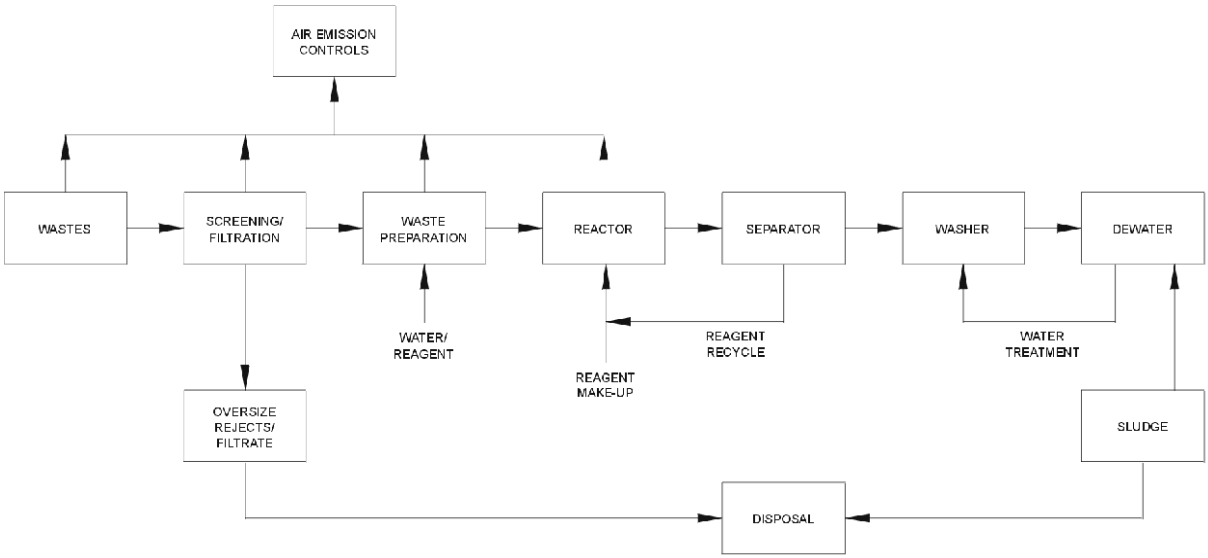

FIGURE 18-1. TYPICAL PROCESS FOR CHEMICAL REDUCTION/OXIDATION PROCESS

c. Resulting Waste Streams.

The technology produces three streams that may require additional handling:

- Emissions from soil excavation (requires additional treatment).
- Effluent water from dewatering (may be recycled or may be discharged after treatment).
- Sludge and oversized rejects (may require additional treatment prior to disposal).

If the process is not optimized, formation of intermediate contaminants or incomplete oxidation (such as organic acids or aldehydes) may occur.

For additional information on similar processes, see Chapters 15 and 16.

18-3. Hazard Analysis

Principal unique hazards associated with chemical reduction/oxidation, methods for control, and control points are described below.

a. Physical Hazards.

(1) *Incompatible Treatment Materials and Reagents.*
Description. Because of the reactive nature of the chemical reagents (e.g., sulfuric acid, ozone, hypochlorites), system components must be compatible with the reagents, waste stream, and treatment byproducts. System incompatibility may result in fires, system over-pressurization, environmental release, or an explosion.

Control. Controls for incompatible treatment materials and reagents include:

- Train operators in the site and process-specific chemical and physical hazards that will be encountered.
- Perform a Process Hazard Analysis (PHA) prior to startup and correct all deficiencies found.
- Use liquid transfer equipment (pumps, piping, pipe fittings, valves, and instruments) that are chemically resistant to the liquid streams. Use EM 1110-1-4008, "Liquid Process Piping," for materials selection.
- Identify all tanks, drums, and chemical transfer equipment in accordance with 29 CFR 1910.1200 requirements.
- Utilize automatic alarm systems (e.g., pH, temperature, pressure, reactant off-gas concentration detectors) with sensors installed at critical points throughout the system to monitor all phases of the reactions.
- Implement appropriate chemical storage and handling procedures to prevent contact or mixture of incompatible reagents or materials.
- Use secondary containment systems for drums containing hazardous chemicals exceeding reportable quantities, and recommend use of secondary containment systems for hazardous chemicals not exceeding reportable quantities but that continue to pose a risk to the workers or environment.
- During construction, the design engineer must authorize all equipment and material substitutions.
- Train operators in emergency procedures in the event of a catastrophic failure, in life saving first aid procedures including halting chemical reactions, extracting, decontaminating and stabilizing victims, and in emergency system isolation and shutdown procedures.

CONTROL POINT: Design, Construction, Maintenance

(2) *Uncontrolled Reactions.*

Description. Improper chemical handling, e.g., mixing concentrated acids or bases without sufficient cooling or dilution, may generate excessive heat and pressure within the system, resulting in out-of-control reactions and fire or explosions.

Control. Controls for reactions include:

- Train operators in proper chemical handling and storage procedures and potential associated chemical reactions and effects.
- Perform a Process Hazard Analysis (PHA) prior to startup and correct all deficiencies found.
- Monitor the injection of reagents.
- Monitor the process temperatures at critical points.
- Provide for automatic feed shutdowns at preset temperatures.
- Train the operators in emergency procedures in the event of a catastrophic failure, in life saving first aid procedures including halting chemical reactions, extracting, and decontaminating and stabilizing victims, and in emergency system isolation and shutdown procedures.

- Locate emergency eyewashes and showers at critical points throughout the system. (See American National Standards Institute ANSI Z358.1 – 1998.)

CONTROL POINT: Design, Operations, Maintenance

(3) *Flushing Agents*.
Description. Treatment and cleaning reagents may be incompatible. Cleaning reagents are often used to flush the system prior to startup. These reagents can be incompatible with any residual treatment reagents (e.g., chlorine, hypochlorites) left in the system. The reaction of these chemicals may cause heat and pressure buildup within the system, possibly resulting in an explosion.

Control. Controls for flushing agents include:
- Train the operators on the process chemistry that will be used, including the heat of reaction, handling, and potential chemical incompatibilities.
- Perform a Process Hazard Analysis (PHA) prior to startup and correct all deficiencies found.
- Train the operators in emergency procedures to implement in the event of a catastrophic failure, in life saving first aid procedures including halting chemical reactions, extracting, decontaminating and stabilizing victims, and in emergency system isolation and shutdown procedures.
- Locate, install, and maintain emergency eyewashes and showers at critical points throughout the system. (See ANSI Z358.1 – 1998.)

CONTROL POINT: Operations, Maintenance

(4) *Plugged Waste Lines*.
Description. Sludge from the chemical reduction/oxidation process may plug pipes if the rate of precipitation exceeds the rate of sludge removal. Plugged lines may result in an explosion from system over-pressurization or fire if the pump motor heats.

Control. Controls for plugged waste lines include:
- Train the operators in the chemistry involved in the sludge system operation, in the heat of reaction of the chemical reactions, in handling and transferring sludge.
- Use auger-equipped waste lines or flow controls.
- Install alarms to alert operators of system over-pressurization.
- Train the operators in emergency procedures in the event of a catastrophic failure, in life saving first aid procedures including halting and neutralizing chemical reactions, extracting, decontaminating and stabilizing victims, and in emergency sludge system isolation and shutdown procedures.
- Locate, install, and maintain emergency eyewashes and showers at critical points throughout the system. (See ANSI Z358.1 – 1998.)

CONTROL POINT: Design, Operations, Maintenance

(5) *Tank Mixing Equipment.*
Description. Tank mixing equipment may splash chemical reagents (e.g., acids or hydrogen peroxide) or entangle workers who come in contact with propellers or shafts.

Control. Controls for mixing equipment include:

- Train operators in the characteristics of the tank mixing equipment, in all potential pinch points and rotating part or splash exposures from the equipment, in the chemistry involved, in the heat of reaction of the chemical, and chemical handling or transfer.
- Use tanks and mixers designed to reduce or prevent splashing or entanglement with shafts or motors.
- Implement lock-out/tag-out procedures when performing maintenance activities on the mixers.
- Train workers in potential chemical contact hazards and control measures (see 29 CFR 1910.1200). Train the operators in emergency procedures in the event of a chemical splash exposure or physical entanglement, in life saving first aid procedures including emergency de-energizing equipment, halting and neutralizing chemical reactions, extracting, decontaminating and stabilizing victims, and in emergency sludge system isolation and shutdown procedures.
- Install, locate, and maintain emergency eyewash/showers at critical points with easy access to the mixing tank equipment. (See ANSI Z 358.1 – 1998.)

CONTROL POINT: Design, Operations, Maintenance

(6) *Electrical Shock.*
Description. Unprotected electrical cables and lines can be damaged by personnel, vehicles, or heavy objects that may split or tear protective insulation. Exposure to electricity in wet or damp areas can result in electrical shock, severe burns, or death.

Control. Controls for electrical shock hazards include:

- Train operators in electrical systems used and potential electrocution hazards.
- Use ground-fault protected electrical systems in areas that could become wet or damp. Electrical system design must follow “National Electrical Code” NFPA 70 and UFGS 16415A, “Electrical Work, Interior.”
- Use grounded or GFIC-protected equipment if required by EM 385-1-1, Section 11, or NFPA 70.
- Perform all electrical work according to code and under the supervision of a state licensed master electrician.
- Never allow the use of unapproved wiring or temporary wiring, such as electrical cords, during maintenance work where contact with water, wet or damp surfaces could be encountered.

- Where possible bundle lines and secure a safe area by using cones, flagging, or mesh fencing to alert workers. Mark bundles with reflective tape for 24 hour per day operations.
- Do not bundle electrical lines with pressure lines.

CONTROL POINT: Design, Construction, Operations, Maintenance

(7) *Emergency Wash Equipment.*
Description. Emergency shower/eyewash equipment required per 19 CFR 1910.151 is not always provided with adequate floor drains, thereby creating potential electrical hazards or walking surface hazards during required testing and use.

Control. A control for emergency wash equipment includes:
- See American National Standards Institute ANSI Z 358.1 – 1998: "Emergency Eyewash and Shower Equipment" for design requirements.
- Equip showers/eyewash equipment with accompanying functional drains to isolate and collect the shower/eyewash water from unprotected electrical equipment and walking surfaces that, when wet, create slipping hazards.

CONTROL POINT: Design

(8) *Confined Spaces*.
Description. Workers who enter permit-required confined spaces, such as process vessels, for inspection and maintenance can encounter serious hazards, including asphyxiation from the lack of oxygen. exposure to toxic chemical vapors and gases; or poisonous gases from the redox reagents such as ozone, hydrogen peroxide, hypochlorites, chlorine, or chlorine dioxide, and treatment contaminants such as cyanide, or chromium-containing wastes, phenols and other readily oxidized organics, and engulfment/entrapment by the treatment slurry.

Control. Controls for confined-space entry include:
- Thoroughly train operators and workers in confined space hazards and safety procedures employed in confined spaces.
- Design redox vessels to maximize ease of operation, cleaning, and maintenance to include accessible, adequately sized access doors or entry ports, and to minimize the frequency, duration, and extent of cleaning and maintenance required.
- Develop a confined space permit program that includes hazard assessment requiring atmospheric testing inside the vessels both prior to and throughout the work planned. (See 29 CFR 1910.146.)
- Ventilate the vessel interior prior to and during entry to eliminate the oxygen-deficient, toxic, or poisonous atmosphere. (The treatment slurry in the redox vessels may exhibit a measurable oxygen deficit creating a oxygen-deficient atmosphere.)

- Complete the vessel manufacturer's shutdown procedures and lock-out/tag-out of associated pumping or electrically energized systems prior to entry. Eliminate possible buildup of static electricity.
- Use air-supplied respirators to control inhalation exposures to toxic chemicals and poisonous gases to prevent any potential for asphyxiation in situations where only constant mechanical ventilation prevents the buildup of a toxic or inert gas environment.

CONTROL POINT: Design, Construction, Operations, Maintenance

(9) *Respirable Quartz Hazard*.
Description. Depending on soil types, exposure to respirable quartz may be a hazard during the excavation phase of the treatment process. Consult geology staff to confirm the presence of a respirable quartz hazard (e.g., to determine if soil types are likely to be rich in respirable quartz). As an aid in determining respirable quartz exposure potential, sample and analyze site soils for fines content by ASTM D422 (R2002): "Standard Test Method for Particle Size Analysis of Soils" followed by analysis of the fines by X-ray diffraction to determine crystalline silica quartz content.

Control. Controls for respirable quartz include:
- Wet soil periodically with water to minimize worker exposure. Wetting of soil may require additional controls to deal with resulting water, ice, mud, etc. Consult 29 CFR 1910.1000, Table Z-3, to calculate acceptable respirable dust concentrations based on percent silica in the quartz.
- Use respiratory protection, such as an air purifying respirator equipped with N, R or P100 particulate air filters.
- Train workers in the potential inhalation hazards of crystalline silica dust exposures.

CONTROL POINT: Design, Construction, Operations, Maintenance

(10) *Design Field Activities*.
Description. Design field activities associated with subsequent construction may include surveying, biological surveys, soil gas surveys, geophysical surveys, trenching, drilling, stockpiling, contaminated groundwater sampling, and other activities. Each of these field activities may expose the survey personnel to physical, chemical, radiological, and biological hazards.

Control. Controls for hazards resulting from design field activities include:
- Prepare an activity hazard analysis for predesign field survey activities. EM 385-1-1, Section 1.A, provides guidance on developing an activity hazard analysis.
- Train workers in hazards identified.

CONTROL POINT: Design

b. Chemical Hazards.

(1) *Chemical Reagents (Use and Storage).*
Description. Treatment workers can be exposed to toxic and reactive chemical reagents such as ozone and hydrogen peroxide. Storage requirements may include heat and moisture content, ambient temperature, or relative humidity. The reagents may deteriorate and react under certain conditions to generate heat and pressure within their storage containers. Mixing incompatible reagents in the reaction tanks may generate toxic vapors (such as hydrogen or chlorine) or generate sufficient heat to ignite combustible materials.

Control. Controls for chemical reagents include:

- Label all tanks and piping systems.
- Store all chemicals and redox reagents in accordance with NFPA, manufacturer, and Material Safety Data Sheet requirements. Do not store a greater chemical inventory than can be used within the acceptable storage period.
- Use temperature and moisture control in storage areas.
- Segregate storage areas by dikes. Ensure dikes do not commingle at drains.
- Use spill control equipment.
- Determine reagent compatibility prior to placement in storage and following their introduction into the system.
- Use the Buddy System and mix all chemical reagents in reaction tanks in accordance with NFPA and manufacturers requirements, employing all prescribed personal protection equipment (PPE), including respirators, face shields, and chemical splash resistant (rubber) suits.
- Install, and maintain emergency eyewash/showers at critical points with easy access to the mixing tank equipment and the chemical storage areas. (See ISEA Z 358.1 – 1998.)
- Consult Material Safety Data Sheets to determine the specific chemical hazards associated with the reagent chemicals and train workers in hazard avoidance techniques (see 29 CFR 1910.1200). Ensure MSDSs are current and meet all OSHA requirements. MSDSs over 3 years old should be renewed.
- Consult NIOSH and other recognized research agencies to augment weak sections of MSDSs, particularly the PPE section.
- Train the operators in the operating characteristics of the tank mixing equipment, splash exposures from mixing reagents, in the chemistry involved, in the heat of reaction and toxicity of the chemical reactions, and handling and transferring the chemicals.
- Train the operators in emergency procedures in the event of a chemical splash or toxic vapor exposure, in life saving first aid procedures including emergency de-energizing equipment, halting and neutralizing chemical reactions, extracting, decontaminating, and stabilizing victims, and in emergency reaction tank system isolation and shutdown procedures.

- Ensure that a Spill Prevention Containment Control (SPCC) Plan is prepared and workers understand how it applies to their job duties.
- Check local and state requirements for the SPCC Plan. Ensure that fire and emergency agencies are aware of the chemical hazards and have access copies of the SPCC as required.

CONTROL POINT: Design, Operations, Maintenance

(2) *Chemical Reagent Exposure*.
Description. Chemical reagents are listed in CEGS 11242, "Chemical Feed Systems." Workers may be exposed to these chemical reagents or to byproducts of chemical reduction/oxidation via the inhalation/ingestion/dermal exposure routes. Materials may be toxic (such as carbon monoxide and chlorine) or explosive (as with hydrogen).

Control. Controls for chemical reagent exposure include:

- Train operators in the characteristics of the mixing equipment, potential splash hazards from mixing reagents, in the chemistry involved, in the heat of reaction and toxicity of the chemical reactions, and in handling and transferring the chemicals.
- Train the operators in emergency procedures in the event of a catastrophic release, chemical splash or toxic vapor exposure, in life saving first aid procedures including emergency de-energizing equipment, extinguishing, halting and neutralizing chemical reactions, extracting, decontaminating, and stabilizing victims, and in emergency reaction tank system isolation and shutdown procedures in accordance with the SPCC Plan.
- Install, and maintain emergency eyewash/showers at critical points with easy access to the mixing tank equipment and the chemical storage areas. (See ANSI Z 358.1 – 1998.)
- Pressure test all piping connections.
- Consult Material Safety Data Sheets to determine the specific health hazards associated with the specific chemical reagents utilized in the process. Material Safety Data Sheets describe the specific personal protective equipment (PPE) required and appropriate neutralization measures in the event of a spill or exposure.
- Test the atmosphere inside tanks prior to each entry (see Paragraph 18-3*a*(8) of this chapter).
- Ventilate the system to prevent the accumulation of hydrogen, chlorine, or other toxic and explosive gases.
- Equip areas where byproducts, such as carbon monoxide, chlorine, and hydrogen, are generated with local exhaust ventilation. If the generation of ozone, CO, Cl_2, or hydrogen is significant and cannot be properly exhausted, install carbon monoxide or hydrogen monitors with visual and audible alarms to alert operators.

CONTROL POINT: Design, Operations, Maintenance

(3) *Improper Chemical Amounts*.
Description. Effluent water may contain significant concentrations of reagents that can cause skin and eye damage. In instances where too much chemical has been used, the residual chemical can cause reactions and high temperatures. The under-use of chemicals can cause incomplete process reactions that may cause over-pressurization of the system and subsequent leaks.

Control. Controls for chemical amounts include:

- Train the operators in the characteristics of over- or under-mixing reagents, in the chemistry involved, in the heat of reaction and toxicity of the chemical reactions resulting from improper mixing, and in handling and transferring the chemicals.
- Use oxidation or reduction mixing/retention tanks with monitors and alarms for chemical dosages or operational temperatures that exceed preset limits.
- Ensure that a Design Analysis includes failure-mode analyses. Include control logic in facility design to shut down chemical transfer systems under upset conditions. Ensure that possible failures and errors trigger shut downs in the safest mode possible, even if it means equipment damage.
- Train the operators in emergency procedures in the event of a dangerous increase in the rate of reaction and temperature or pressure rise, toxic vapor release, in life saving first aid procedures including emergency de-energizing the tanks or transfer equipment, halting and neutralizing chemical reactions, extracting, decontaminating, and stabilizing victims, and in emergency reaction tank isolation and shutdown procedures.

CONTROL POINT: Design, Construction, Operations, Maintenance

(4) *Chemical Reagents (Compatibility).*
Description. Flushing the system prior to startup may cause chemical reactions and increased pressure with the reagents during system operation.

Control. A control for chemical reagents includes:

- Review the compatibility of the chemical reagents used in system operation prior to addition and mixing of these reagents.
- Make Material Safety Data Sheets, in accordance with ANSI 2400.1, available to operators. Ensure that MSDSs are current and meet all OSHA requirements. MSDSs over 3 years old should be renewed.
- Use NIOSH and other authorized research agencies to augment weak sections of MSDSs, especially the PPE section.
- Train operators in the characteristics of the mixing reagents, in the chemistry involved, in the heat of reaction and toxicity of the chemical reactions resulting from improper mixing, handling and transferring the chemicals.

CONTROL POINT: Design, Operations, Maintenance

(5) *Chemical Exposure From Equipment Failure*.

Description. Reactive chemicals used in the process may corrode pipes, gaskets, and connectors, causing leaks and worker exposure. Workers may be exposed to reactive chemical reagents, including hydrogen peroxide, hypochlorites, and chlorine.

Control. Controls for chemical exposure resulting from equipment failure include:

- Ensure that possible failures and errors trigger shut downs in the safest mode possible, even if it means equipment damage.
- Design/construct process equipment with compatible materials. Use EM 1110-1-4008, "Liquid Process Piping," for appropriate selection of materials.
- Feed reagent chemicals automatically into the system via a closed piping system.
- Wear proper PPE for handling the reagents if manual addition is required.
- Train workers in potential chemical hazards and controls (see 29 CFR 1910.1200).

CONTROL POINT: Design, Operations, Maintenance

(6) *Contaminants (Screening Process).*
Description. When screening contaminated materials, employees may be exposed, via dermal or inhalation routes, to soils, sludge, dust, or oversized rejects.

Control. Controls for exposure to contaminants include:

- Use water during soil screening to minimize the amount of dust generated.
- Perform dust monitoring if necessary to determine when respiratory protection, such as air-purifying respirators equipped with N, R or P100 or N, R or P95 particulate air filters, should be donned.
- Wear chemical-resistant coveralls and gloves (match compounds with manufacturers charts on break through times [BTT] and permeation rates) to prevent direct contact with the contaminated soils. Such controls prevent workers from carrying any contamination home on their clothing.
- Ensure work rules include hygiene policies and requirements.
- Ensure that designs include hygiene facilities to meet these requirements. Facilities may include portable showers, change areas and lockers, hand and face wash areas, boot wash areas, and contaminants clothing and PPE drop-off stations.
- Ensure that clean PPE, such as respirators and suits, are stationed for easy access before entering dust or chemical hazard areas.

CONTROL POINT: Operations

c. Radiological Hazards.

Radioactive Devices.

Description. Fire ands smoke detection devices, fluid level devices and other process monitors and switches may contain radioactive devices potentially exposing workers through lack of identification or mishandling.

Control. Controls for inadvertent handling or exposure to radioactive devices include:

- Workers should be prevented from and warned against tampering with the devices.
- The location of the devices should be recorded so as to safely retrieve and dispose of them in case of a system failure and equipment replacement.

CONTROL POINT: Design, Operations and Maintenance

d. Biological Hazards.

Opportunistic Insects and Animals.
Description. For all sites but especially in cooler climates, opportunistic insects or animals can nest in and around warm process equipment. Vermin, insect, and arthropod control measures should be considered in any design.

Control. Control of opportunistic insect and animals include:

- Electrical cabinets and other infrequently opened enclosures should be opened carefully and checked for black widow and brown recluse spiders, and evidence of rodents. As rodents can cause damage to electrical cables, all wiring should be inspected regularly.
- Ensure all storage is off the ground, palleted, and kept dry. Damp areas attract scorpions, rodents, and the snakes that eat them.
- Design ceiling corners and other high areas to discourage nesting by swallows, pigeons, and other birds. Birds are carriers of diseases, especially in their droppings, which can foul process equipment.

CONTROL POINT: Design, Operations and Maintenance